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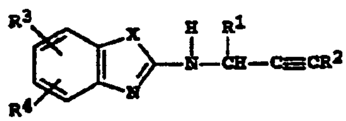
(54) Abstract Title

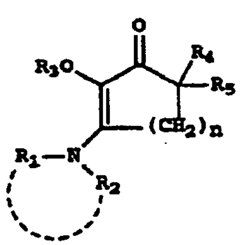
Image stability using alkynylamines, reductones and iodide emulsions

(57) A photographic element wherein at least one layer comprises silver halide grams wherein said grains have a surface iodide of less than 1 mol percent, total grain iodide of about 0.5 to 10 mol percent, said iodide being located in the core of the grains, an alkynylamine compound of Formula I:



I

wherein X is O, S, SE, oxygen, sulfur, selenium, or an unsubstituted or alkyl substituted N; R^1 is H, or alkyl of from 1 to 5 C atoms, and R^2 is H, hydrogen, or alkyl, aryl, heteroaryl, carbocyclic or heterocyclic group, and R^3 and R^4 independently are H, halogen, or a substituted or unsubstituted alkyl or alkoxy group, and the reductone of Formula II



II

wherein R_1 and R_2 are the same or different, and may represent H, alkyl, cycloalkyl, aryl, or an alkyl group with a solubilizing group such as -OH, sulfonamide, sulfamoyl, or carbamoyl, R_1 and R_2 may be joined to complete a heterocyclic ring, R_4 and R_5 are H, OH, alkyl, aryl, cycloalkyl, or may together represent an alkylidene group, n is 1 or 2 and R_3 is H, alkyl, aryl, or CO_2R_6 where R_6 is alkyl. The element is preferably multicolour and stabilises latent images.

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LATENT IMAGE STABILITY USING ALKYNYLAMINES AND IODIDE EMULSIONS

FIELD OF THE INVENTION

This invention relates to the use of alkynylamines with a photographic emulsion to obtain optimum latent image stability in a given color film format.

BACKGROUND OF THE INVENTION

The ability to maintain a latent image is of paramount importance to commercial photographic products. Customers typically make exposures on a roll of film over a period of time which can range up to several months from the first to the last exposure. These latent images are then processed together and should produce dye densitites in color film independent of exposure age for optimum color reproduction. Complete maintainence of the latent image under these conditions is rarely achieved in the complex chemical milleau consitituting a color film. Rather, ways have been sought to minimize its loss and thereby deliver to the customer the most consistent color reproduction possible.

A variety of latent image stabilizers have been described (Herz, U.S. Patent 4,374,196) with notable success achieved by derivatives of N-2-alkynylaminobenzothiazolium salts (Lok et al, U.S. Patent 4,451,557 and U.S. Patent 4,378,426 and Eikenberry et al, U.S. Patent 5,500,333). Although these materials showed good success in reducing latent image loss, they were examined in single color, single layer formats considerably simpler than the complex, tri-color, multi-layer format needed for complete and accurate color reproduction.

The translation of single layer latent image stability to multi-layer performance is often frustrated by unexpected offsets and chemical interactions. Furthermore, a multi-layer format will evolve during the development of a new commercial film for a variety of reasons: to gain improved color reproduction through inter-image effects; to improve the chemical stability prior to exposure; to reduce sensitivity to variable processing factors; or for a variety of other reasons.

This evolution usually involves a shift in the chemical and/or physical make up of the multi-layer film that brings with it a change in the requirements needed to obtain latent image stability. For example, a combination of emulsion and addenda that gave good performance in a single layer or in the initial multi-layer format may prove insufficient as the format evolves.

PROBLEM TO BE SOLVED BY THE INVENTION

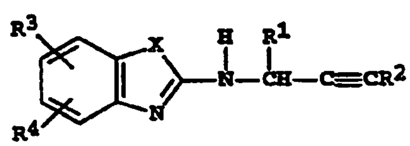
There is, thus, a need for a technique of applying adjustable latent image stability that can be customized to a particular format. There is a need for improvement in latent image stability, particularly in photographic elements utilizing reductones.

SUMMARY OF THE INVENTION

It is an object of the invention to provide photographic elements having improved latent image stability.

Another object of the invention is to provide a means of obtaining the optimum stabilization of the latent image for a given color multi-layer film format by adjusting the addenda used in the chemical sensitization.

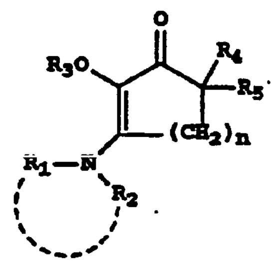
These and other objects of the invention generally are accomplished by a photographic element wherein at least one layer comprises silver halide grains wherein said grains have a surface iodide of less than 1 mol percent, total grain iodide of about 0.5 to 10 mol percent, said iodide being located in the core of the grains, an alkynylamine compound having Formula I:



I

wherein X represents oxygen, sulfur, selenium, or an unsubstituted or alkyl substituted nitrogen; R^1 represents hydrogen or an alkyl of from 1 to 5 carbon atoms, and R^2 represents hydrogen, or an alkyl, aryl, heteroaryl, carbocyclic or heterocyclic group, and R^3 and R^4 independently represent hydrogen, halogen, or

a substituted or unsubstituted alkyl or alkoxy group, preferably one having fewer than 6 carbon atoms, and the reductone of Formula II



II

wherein R_1 and R_2 are the same or different, and may represent H, alkyl, cycloalkyl, aryl, or an alkyl group with a solubilizing group such as -OH, sulfonamide, sulfamoyl, or carbamoyl, R_1 and R_2 may be joined to complete a heterocyclic ring, R_4 and R_5 are H, OH, alkyl, aryl, cycloalkyl, or may together represent an alkylidene group, n is 1 or 2 and R_3 is H, alkyl, aryl, or CO_2R_6 where R_6 is alkyl, and

wherein the logarithm of the partition coefficient for the reductone when equilibrated as a solute between n-octanol and water (logP) is less than 0.293.

In another embodiment of the invention there is shown a photographic element comprising at least one yellow dye forming blue sensitive layer, at least one cyan dye forming red sensitive layer, and at least one magenta dye forming green sensitive layer wherein at least one of said layers comprises silver halide grains wherein said grains have a surface iodide of less than 1 mol percent, a total grain iodide of about 0.5 to 10 mol percent, said iodide being located in the core of the grains, an alkynylamine compound of Formula I and the reductone of Formula II.

ADVANTAGEOUS EFFECT OF THE INVENTION

The invention has the advantage of allowing the orignator of a new color film to adjust the latent image stabilization in a predictable manner as the film composition evolves. The convenient selection of the emulsion/addenda combination giving optimum latent image stabilization simplifies the work needed to insure that the customer will obtain the most consistent color reproduction of prints from a roll of film exposed over a period of time.

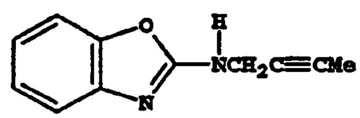
DETAILED DESCRIPTION OF THE INVENTION

The invention has numerous advantages over prior photographic elements in exhibiting both raw storage stability and latent image keeping ability. The photographic elements of the invention by the combination of additives may be adjusted to exhibit exceptional latent image stability while also being raw storage stable.

Any suitable alkynylamine compound may be utilized in the invention. Suitable is an alkynylamine compound of Formula I.

Specific compounds contemplated to be suitable as the alkynylamine compound of the invention include:

Compound IA:



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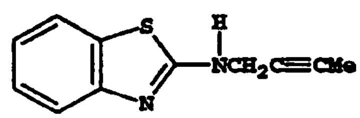
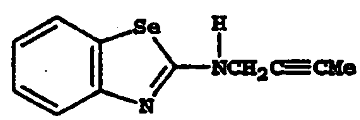


Compound IC:



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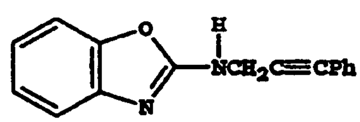
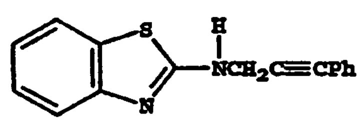
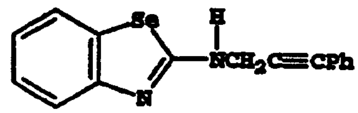


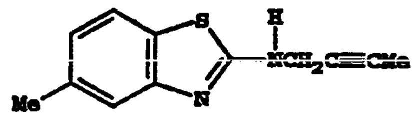
Compound IE:



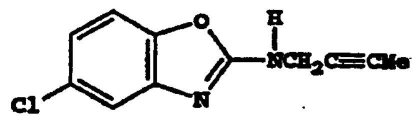
Compound IF:



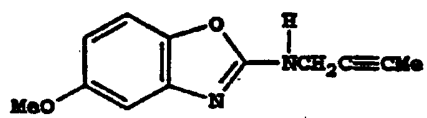
Compound IG:



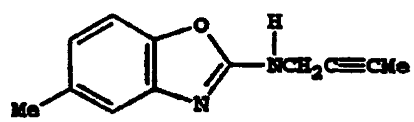
Compound IH:



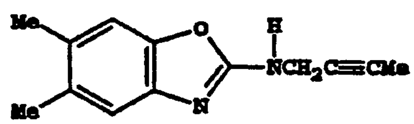
Compound II:



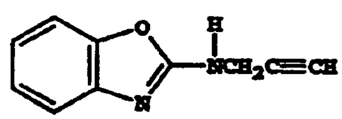
Compound IJ:



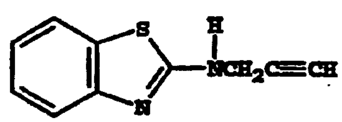
Compound IK:



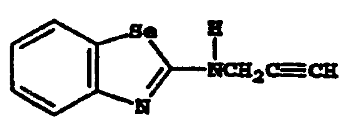
Compound IL:



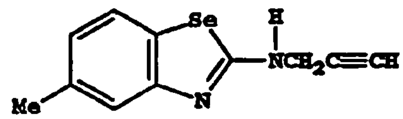
Compound IM:



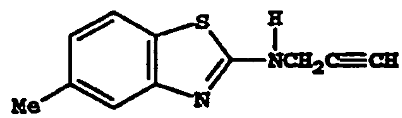
Compound IN:



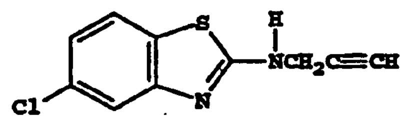
Compound IO:



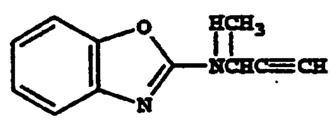
Compound IP:



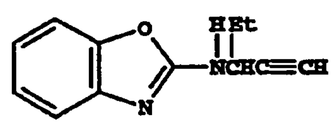
Compound IQ:



Compound IR:

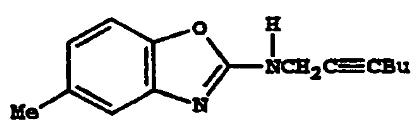


Compound IS:



and

Compound IT:



In the practice of the invention, it is also contemplated that the alkynylamine compound be water soluble; that is, that it further comprise a water solubilizing group. In this embodiment, the water solubilizing group can be substituted anywhere on the alkynylamine (e.g., as a substituent on R^3 or R^4). Preferably, it should be sufficient to enable the alkynylamine to be soluble at 0.1 grams per liter of water. Representative solubilizing groups include carboxy, carboxyalkyl, sulfo, sulfoalkyl, phosphato, phosphatoalkyl, phosphono, phosphonoalkyl, carbonamido, sulfonamido, hydroxy, and salts thereof. Preferably, the water solubilizing group is a carboxy or sulfo group, or salt thereof. Optimally, it is the sodium or potassium salt of a carboxy group.

The alkynylamine compounds utilized in the invention may be prepared by any methods known in the art. Examples of such methods can be found in U.S. Patents 4,451,557; 4,378,426; and 5,413,905, all of which are incorporated herein by reference.

The photographic emulsions employed in this invention are generally prepared by precipitating silver halide crystals in an aqueous colloidal medium (matrix) by methods conventional in the art. The colloid is typically a hydrophilic film forming agent such as gelatin, alginic acid, or derivatives thereof.

The crystals formed in the precipitation step are washed and then chemically and spectrally sensitized by adding spectral sensitizing dyes and chemical sensitizers, and by providing a heating step during which the emulsion temperature is raised, typically from 40°C to 70°C, and maintained for a period of time. The precipitation and spectral and chemical sensitization methods utilized in preparing the emulsions employed in the invention can be those methods known in the art.

Chemical sensitization of the emulsion typically employs sensitizers such as sulfur-containing compounds, e.g., allyl isothiocyanate, sodium thiosulfate and allyl thiourea; reducing agents, e.g., polyamines and stannous salts; noble metal compounds, e.g., gold, platinum; and polymeric agents, e.g., polyalkylene oxides. As described, heat treatment is employed to complete chemical sensitization. Spectral sensitization is effected with a combination of dyes, which are designed for the wavelength range of interest within the visible or infrared spectrum. It is known to add such dyes both before and after heat treatment.

After spectral sensitization, the emulsion is coated on a support. Coating techniques known in the art include dip coating, air knife coating, curtain coating and extrusion coating.

For the purpose of improving the sensitivity of the emulsion, the alkynylamine compounds of the invention may be added to the silver halide emulsion at any time during the preparation of the emulsion. Preferably, they are added during the latter half of grain growth, during or before chemical sensitization or during final melting and co-mixing of the emulsion and additives for coating. It is most desired that the compounds be added prior to the heating step of chemical sensitization.

The alkynylamine compounds can be introduced to the emulsion at the appropriate time by any means commonly practiced in the art such as by dissolving in a convenient organic solvent, or by dispersing in a gelatin matrix.

They may be added to the coupler melt which may be either dualed or combined with the emulsion melt during the coating process; to the vessel containing the aqueous gelatin salt solution before the start of the precipitation; or to a salt solution during precipitation. Other modes are also contemplated. Temperature, stirring, addition rates and other precipitation factors may be set within conventional ranges, by means known in the art, so as to obtain the desired physical characteristics.

The alkynylamine compounds can be incorporated into the emulsion in an amount between about 0.1 and about 200 milligrams per mole of silver halide. When the compounds are added during the precipitation of the emulsion's grains, they are preferably added in an amount between 1 and about 200 milligrams per mole of silver halide. When added during sensitization, it is more preferred to use a lesser amount, typically in the order of 0.1 to 100 milligrams per mole of silver halide. After sensitization, it is preferable to use an amount of the alkynylamine compound between about 1 and 200 milligrams per mole of silver halide.

In addition to the alkynylamine compounds, the present invention's photographic elements incorporate a sulfohydroxy aryl compound. It is this sulfohydroxy aryl compound which surprisingly has been found to counter the fogging deficiencies inherent in the use of the alkynylamines, particularly when it is added to the emulsion prior to the addition of the alkynylamine and prior to the heating step of chemical sensitization. Further, the combination of the two compounds also provides for an increase in sensitivity that could not have been expected based upon the known individual effects of each compound.

The photographic element may also contain a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support, as in U.S. Patents 4,279,945 and 4,302,523 and Research Disclosure, November 1993, Item 3490, which are incorporated herein by reference. Typically, the element will have a total thickness (excluding the support) of from about 5 to about 30 microns.

Any suitable reductone compound may be utilized in the invention. The reductones of the invention can be represented by Formula II. The invention finds its preferred use in improving the performance of color negative films.

The following examples illustrate the practice of this invention. They are not intended to be exhaustive of all possible variations of the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLES

In simple single layer formats where only one emulsion is coated, the measurement of latent image stability is usually done by referencing the photographic speed of an aged latent image against that of a fresh latent image on the same lot of film. Typically, a speed loss is observed as shown by Example 1 in Table 1.

TABLE 1

Effect of Emulsion Type and Additives on Latent Image Stability

Coating	Emulsion	Additive	Amount (mg/mole)	Speed Change Single Layer*	Density Change Multi-layer**
Example 1	A	none	-	- 13	
Example 1a	A	none	-		-0.058
Example 2	A	IL	2	- 8	
Example 2a	A	IL	2		-0.025
Example 3	B	none	-	-15	
Example 3a	B	none	-		-0.039
Example 4	B	IL	2	-17	
Example 4a	B	IL	2		-0.010
Example 5	C	none	-	-4	
Example 5a	C	none	-		+0.006
Example 6	C (invention)	IA	3	-4	
Example 6a	C (invention)	IA	3		+0.024

*Speeds were measured as 100(1-logH) where H is the exposure in lux-sec necessary to produce a density 0.15 above Dmin. Speed changes in a single layer were measured by first exposing a sample and then holding the sample for 1 week at 120F/50% RH before performing the usual C-41 process. The speed from this

*Speeds were measured as 100(1-logH) where H is the exposure in lux-sec necessary to produce a density 0.15 above Dmin. Speed changes in a single layer were measured by first exposing a sample and then holding the sample for 1 week at 120F/50% RH before performing the usual C-41 process. The speed from this aged sample was then compared to the speed obtained from a control sample which was exposed and immediately processed with the aged sample.

**Density changes in the multi-layer were obtained by aging unexposed film for 3 weeks at 100F/50% RH, exposing the film and then holding one more week at 100F/50% RH before processing. The control in this case was a film strip held 4 weeks at 100F/50% RH which was then exposed and immediately processed with the sample containing the aged latent image. Density was measured at step 11 in a 21 step tablet which corresponds to the region in the density vs. exposure curve dominated by the emulsion of interest.

In a multi-layer format where several emulsions are coated to obtain a wide exposure latitude, it is often difficult or impossible to measure the exact photographic speed of only one emulsion. Therefore, emulsion performance under these circumstances is often done by comparing dye densities at a given exposure. For example, the single layer speed loss of -13 observed for Emulsion A in Example 1 in Table 1 translates to a density loss of -0.058 in Example 1a in a multi-layer environment.

When additive IL is added to Emulsion A after chemical sensitization as suggested by Lok et al in U.S. Patent 4,451,557 the single layer latent image stability is improved as reflected by the smaller speed loss shown for Example 2 in Table 1. Likewise, the smaller density loss in Example 2a in the multi-layer format also indicates better latent image stability.

In the case of Examples 3 and 4 employing Emulsion B which is a smaller version of Emulsion A, the addition of IL did not appear to improve latent image stability as shown by the similar speed losses observed in the presence and absence of Ia (Example 4 vs. 3 in Table 1). However, when coated in a multi-layer

format, this comparsion does show improved latent image stability as reflected by the smaller density loss for Example 4a vs 3a. This case illustrates the importance of evaluating latent image stability in the full film format to be used in the final product.

Although the addition of IL enhanced latent image stability, density losses in the multi-layer are still observed in Examples 2a and 4a and there remains a need for more improvement. We have made the unexpected observation that a modification of the iodide structure of the conventional run/dump emulsion (Johnson and Wightman, U.S. Patent 5,164,292) utilized by emulsions A and B can greatly improve the latent image stability. For example, Emulsion C in Table 1 is essentially the same as Emulsion B except that the iodide dump step in the preparation of Emulsion B has been omitted and the % iodide run into the kettle during the first part of the make has been increased to compensate for the iodide not added in the dump. A significant feature of this procedure change is the reduction of surface iodide from 5 mol % in Emulsion B to 0.2 mol % in Emulsion C. The result of this change in iodide structure on latent image stability can be seen in Example 5 and 5a vs. 3 and 3a where the single layer speed loss is greatly reduced and the multi-layer density change is very small, even showing a slight gain. With the addition of alkynylamine IA the multi-layer density change becomes even more positive as seen for Example 6a.

Although the the gain in density seen for Example 6a would be as detrimental to color reproduction as the loss in density observed in Example 2a, we find this behavior to be a potential advantage as the multi-layer format evolves. For instance, as shown in U.S. Application Serial No. 08/814,517 filed March 10, 1997, the addition of piperidino hexose reductone (PHR) to the multi-layer format has been observed to greatly improve the stability of the film prior to exposure, but it degrades the stability after exposure (the latent image) as seen in Table 2.

TABLE 2

Effect of PHR on Latent Image Stability in a Color Negative Film

Coating	Emulsion	Additive	Amount (mg/mol)	Density Change Multi-Layer* (-)PHR	Density Change Multi-Layer* (+)PHR
Example 2a	A	IL	2	-0.025	
Example 2b	A	IL	2		-0.048
Example 4a	B	IL	2	-0.010	
Example 4b	B	IL	2		-0.021
Example 6a	C (invention)	IA	3	+0.024	
Example 6b	C (invention)	IA	3		-0.014

*See Table 1 for definition of density change.

In every case in Table 2 the density differences observed in the absence of PHR became more negative with the addition of PHR. The positive bias for Example 6a then becomes a smaller negative bias in Example 6b than what is observed for the usual combination of emulsion and alkynylamine in Example 4b.

The improved performance for the combination of a run iodide emulsion and alkylnylamine in the presence of PHR is further illustrated in Table 3 where the emulsions were compared in pilot coatings for production. The combination in Example 8 which constitutes the invention is clearly producing better latent image stability than Example 7 which utilizes the conventional combination of emulsion and alkynylamine.

TABLE 3
Latent Image Stability of Emulsion/Alkynylamine Combinations

Coating	Emulsion	Additive	Amount (mg/mole)	Density Change Multi-layer*
Example 7	B	IL	2	-0.056
Example 8	C (invention)	IA	3	-0.021

*See Table 1 for definition of density change.

The unexpected advantage of the invention is clearly illustrated when the effect of adding different levels of IL to the conventional run/dump emulsion (Emulsion B) after chemical ripening vs. adding IA to Emulsion C (the invention) before chemical ripening.

TABLE 4

Latent Image Stability of Conventional Emulsion/Alkynylamine Combinations vs. that of the Invention

Coating	Emulsion	Additive	Amount (mg/mole)	Speed Change *
Example 9	B	IL	1	-9
Example 10	B	IL	2	-11
Example 11	B	IL	3	-8
Example 12	B	IL	4	-7
Example 13	C (invention)	IA	1	-6
Example 14	C (invention)	IA	2	0
Example 15	C (invention)	IA	3	2
Example 16	C (invention)	IA	4	5

*See Table 1 for the definition of speed changes. For convienent comparison, emulsions were coated singly as the only yellow emulsion in the blue record of a multi-layer film. Data obtained in the presence of PHR.

The unique performance of the invention is seen in the progression of speed changes in Table 4 from negative to positive whereas speed changes for the control remain negative.

Attempts to improve the performance of the conventional run/dump emulsion by adding either IL or IA to Emulsion B before or after chemical ripening failed to significantly improve latent image stability as shown in Table 5. This data demonstrate that the elimination of the latent image speed loss characteristic of a

color negative multi-layer format is uniquely performed by the combination of the modified run/dump emulsion and an alkynylamine.

TABLE 5

Latent Image Stability of a Conventional Run/Dump Emulsion in Combination with Different Alkynylamines

Coating	Emulsion	Additive	Point of Addition	Amount (mg/mole)	Speed Change*
Example 17	B	IL	before	2	-7
Example 18	B	IL	after	2	-7
Example 18	B	IA	before	2	-10
Example 19	B	IA	after	2	-10
Example 20	B	IA	after	4	-11

*See Table 1 for the definition of speed changes. For convenient comparison, emulsions were coated singly as the only yellow emulsion in the blue record of a multi-layer film. Data obtained in the presence of PHR.

EMULSION PREPARATION

Emulsion A

Emulsion A is a tabular grain, bromoiodide emulsion containing 4% iodide. It is in the class described as run/dump and was prepared according to the procedure described by Johnson and Wightman in U.S. Patent 5,164,292. For the first 70% of the make, iodide was added uniformly at the rate of 1.5% of the silver halide being added. When 70% of the total silver had been added, silver iodide was dumped into the making kettle in the amount of 3% of the total silver halide that would be added. An outer shell of silver bromide was then applied to complete the make. The emulsion was prepared at a temperature of 75°C and employed 5 mmol of ammonia/mole of total silver in a 10 min digest immediately following nucleation. The emulsion size was 2.69 x 0.13 μm.

Emulsion B

This emulsion was prepared in a manner similar to A except the making temperature was 54°C and 32 mmol of ammonia/mole of total silver was used in the digest which lasted 2.5 min. The emulsion size was 1.43 x 0.12 μm.

Emulsion C

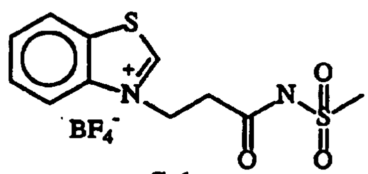
Emulsion C is a tabular grain emulsion, bromoiodide emulsion containing 2.8% iodide. It belongs to the class known as run iodide and was prepared in a manner similar to A except the silver iodide dump was eliminated and the iodide added during the first 70% of the make was increased to 4% of the silver halide being added. The emulsion size was 1.84 x 0.12 μm.

EMULSION SENSITIZATION

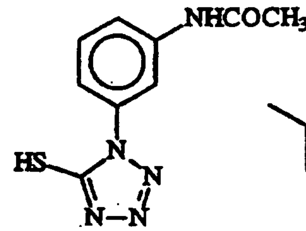
The chemical sensitization of each emulsion was formulated to give the optimum speed/fog performance. Amounts shown are what would be added to 1 mole of emulsion.

Example 1

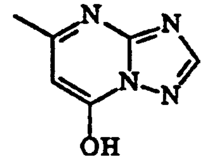
Emulsion A was treated with the following: 100 mg of sodium thiocyanate, 40 mg of finish modifier (S-1), 0.8 mmol of sensitizing dyes consisting of equimolor parts D-1 and D-2, 20 mg of a mercaptotetrazole antifoggant (S-2), 2.5 mg of sodium aurous dithiosulfate, and 1.25 mg of sodium thiosulfate. The mixture was chemically ripened at 65.5°C for 5 minutes and then treated with 1250 mg of tetraazaindene (S-3). The emulsion was coated in a simple, single layer format.



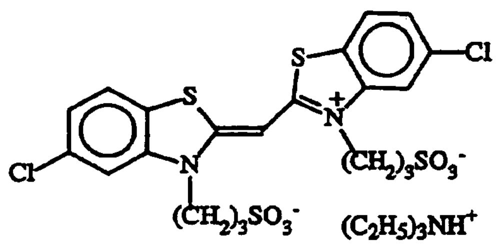
S-1



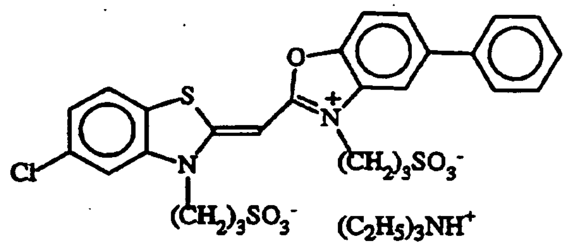
S-2



S-3



D-1



D-2

Organic Additives

Example 1a

Example 1a is identical to Example 1 except the emulsion was coated in a multi-layer format.

Example 2

Emulsion A was treated as in Example 1 except that after chemical ripening, the emulsion was treated with 2 mg of IL, 0.96 mg gold sulfide, and 1250 mg of S-3. The emulsion was coated in a simple, single layer format.

Example 2a

Example 2a is identical to Example 2 except the emulsion was coated in a multi-layer format.

Example 2b

Example 2b is identical to Example 2 except PHR has been added to the multi-layer coating.

Example 3

Emulsion B was treated with the following: 60 mg of sodium thiocyanate, 35 mg of S-1, 0.8 mmol of sensitizing dyes consisting of equimolor parts D-1 and D-2, 15 mg of S-2, 2.5 mg of sodium aurous dithiosulfate, and 1.25 mg of sodium thiosulfate. The mixture was chemically ripened at 67°C for 5 minutes then treated with 2620 mg of S-3. The emulsion was coated in a simple, single layer format.

Example 3a

Example 3a is identical to Example 3 except the emulsion was coated in a multi-layer format.

Example 4

Emulsion B was treated as in Example 2 except that after chemical ripening, the emulsion was treated with 2620 mg of tetraazaindene, 2 mg of IL, and 0.24 mg gold sulfide. The emulsion was coated in a simple, single layer format.

Example 4a

Example 4a is identical to Example 4 except the emulsion was coated in a multi-layer format.

Example 4b

Example 4b is identical to Example 4a except PHR has been added to the multi-layer coating.

Example 5

Emulsion C was treated with the following: 100 mg of sodium thiocyanate, 1.1 mmol of sensitizing dyes consisting of equimolor parts D-1 and D-2, 4.5 mg of sodium aurous dithiosulfate, and 2.25 mg of sodium thiosulfate, and

40 mg of S-1. The mixture was chemically ripened at 68°C for 5 minutes and then treated with 1250 mg of S-3. The emulsion was coated in a simple, single layer format.

Example 5a

Example 5a is identical to Example 5 except the emulsion was coated in a multi-layer format.

Example 6

Emulsion C was treated as in Example 5 except 3 mg of IA was added immediately after D-2. The emulsion was coated in a simple, single layer format.

Example 6a

Example 6a is identical to Example 6 except the emulsion was coated in a multi-layer format.

Example 6b

Example 6b is identical to Example 6a except PHR has been added to the multi-layer coating.

Example 7

Example 7 is identical to Example 4b except the coating experiment was done on production scale.

Example 8

Example 8 is identical to Example 6b except the coating experiment was done on production scale.

COATING EVALUATION

Single Layer

The emulsion was coated in a simple, single layer format over a pad of gelatin on a clear cellulose acetate support with a gelatin overcoat to protect the coating from abrasion. The emulsion layer contained an image forming coupler, Y-1, and an image modifying coupler, DIR-4, both producing a yellow dye.

Multi-layer

The emulsion was coated with couplers Y-1 and DIR-4 in the blue recording layer of a conventional color negative film consisting of red, green and blue sensitive layers coated over an antihalation layer on a clear cellulose acetate support. The multi-layer contained interlayers as needed to modify inter-image effects and had a UV absorbing layer coated last to eliminate UV absorption and protect against abrasion.

The multilayer color negative film elements were constructed using the following layer order:

Support
Layer 1 (AHU, Antihalation U-coat)
Layer 2 (Slow cyan imaging layer)
Layer 3 (Mid cyan imaging layer)
Layer 4 (Fast cyan imaging layer)
Layer 5 (Interlayer)
Layer 6 (Slow magenta imaging layer)
Layer 7 (Mid magenta imaging layer)
Layer 8 (Fast magenta imaging layer)
Layer 9 (Yellow filter layer)
Layer 10 (Slow yellow imaging layer)
Layer 11 (Fast yellow imaging layer)
Layer 12 (Ultraviolet protection layer)
Layer 13 (Protective overcoat)

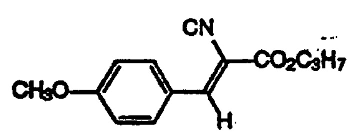
The general composition of the multilayer coatings follows. The examples cited herein specify changes made in layer 10. Layers 1 through 9 and layers 11 and 13 are common throughout for the described multilayer coatings.

Layer	Amount	Component
Layer 1:	2045 mg/m^2	Gelatin
	134.5	Gray Silver
	30.1	UV Absorber dye (DYE-1)
	45.2	UV Absorber (DYE-2)
	21.5	Magenta dye (DYE-3)
	26.9	Cyan dye (DYE-4)
	0.032	Yellow-colored magenta coupler (MC-1)
	0.14	Oxidized developer scavenger (OxDS-1)
Layer 2	1679 mg/m^2	Gelatin
	775	Slow cyan silver
	532.8	Cyan dye former (C-1)
	26.9	Cyan image modifier (DIR-2)
	56.5	Cyan bleach accelerator (B-1)
	32.3	Magenta-colored cyan coupler (MC-2)
Layer 3	1076 mg/m^2	Gelatin
	430.5	Mid cyan silver
	180.8	Cyan dye former (C-1)
	19.4	Cyan image modifier (DIR-2)
	8.1	Cyan bleach accelerator (B-1)
	32.3	Magenta-colored cyan coupler (MC-2)
Layer 4	914.9 mg/m^2	Gelatin
	592.0	Fast cyan silver
	209.9	Cyan dye former (C-1)
	26.9	Cyan image modifier (DIR-2)
	21.5	Magenta-colored cyan coupler (MC-2)
Layer 5	538	Gelatin
	86.1	Oxidized developer scavenger (OxDS-1)
Layer 6	1076 mg/m^2	Gelatin
	430.5	Slow magenta silver
	279.9	Magenta dye former (M-1)
	86.1	Yellow-colored magenta coupler (MC-3)
	10.7	Yellow image modifier (DIR-3)
Layer 7	699.7	Gelatin
	538.2 mg/m^2	Mid magenta silver
	96.9	Magenta dye former(M-1)
	118.4	Yellow-colored magenta coupler (MC-3)
	43.1	Yellow image modifier (DIR-3)

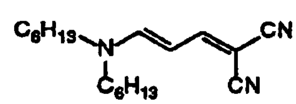
Layer 8	699.7 mg/m^2	Gelatin
	538.2	Fast magenta silver
	70.0	Magenta dye former(M-1)
	53.8	Yellow-colored magenta coupler (MC-3)
	3.3	Cyan bleach accelerator (B-1)
	30.1	Cyan image modifier (DIR-1)
Layer 9	645.8 mg/m^2	Gelatin
	86.1	Oxidized developer scavenger (OxDS-1)
	53.8	YFD-1
Layer 10	807 mg/m^2	Gelatin
	1873.0	Slow yellow silver
	893.0	Yellow dye former (Y-1)
	75.0	Yellow image modifier (DIR-4)
	32.0	Cyan dye former (C-1)
	32.0	Cyan image modifier (DIR-2)
	22.0	Cyan bleach accelerator (B-1)
Layer 11	807 mg/m^2	Gelatin
	517.0	Fast yellow silver
	237.0	Yellow dye former (Y-1)
	75.0	Yellow image modifier (DIR-4)
	5.0	Cyan bleach accelerator (B-1)
Layer 12	699.7 mg/m^2	Gelatin
	107.6	UV absorber dye (DYE-1)
	215.3	Lippmann silver
Layer 13	882.6 mg/m^2	Gelatin
	107.6	Soluble matte beads
	Lubricants	
	1.8% Hardener	

The following structures were used in the multilayer examples:

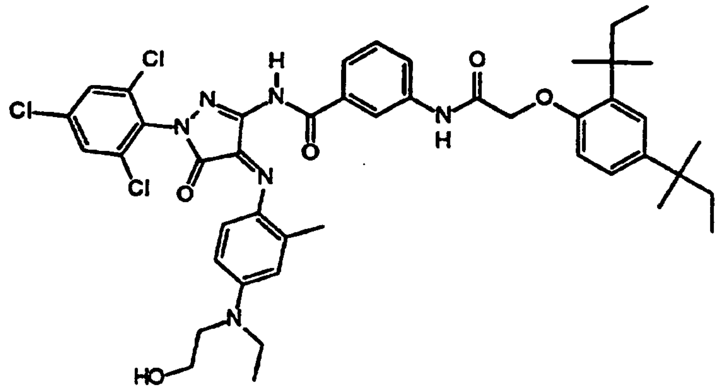
DYE-1



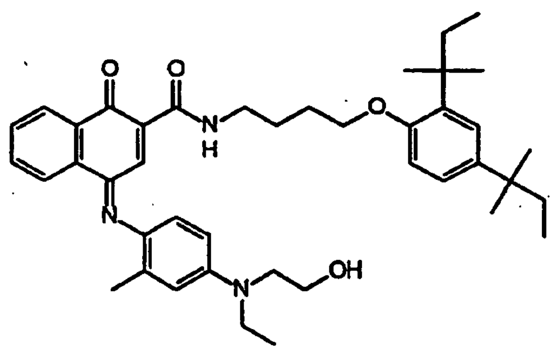
DYE-2



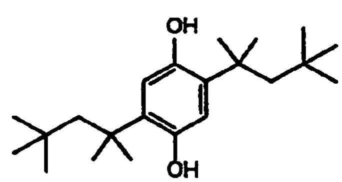
DYE-3



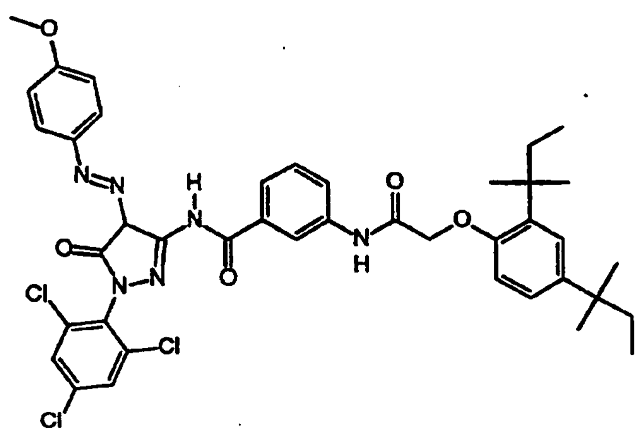
DYE-4



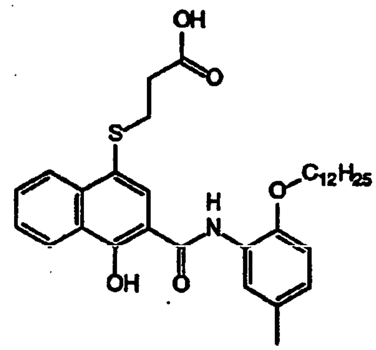
OxDS-1



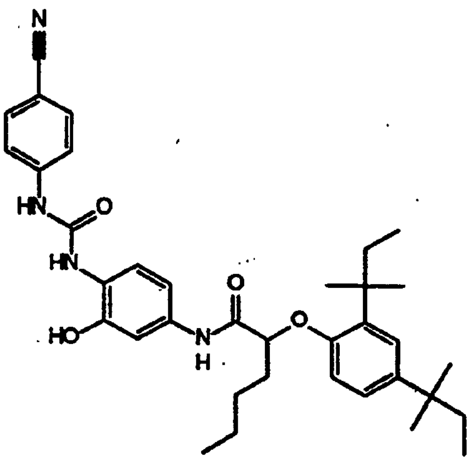
MC-1



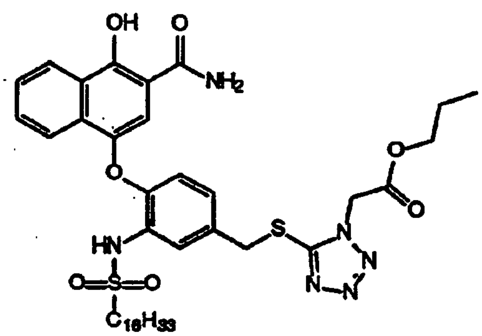
B-1


OH
O
S
O
C12H25
H
N
OH
O

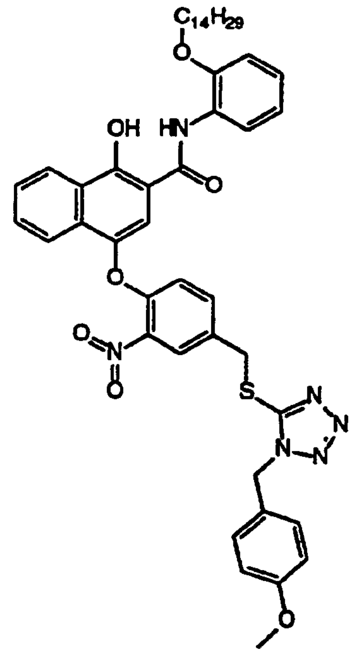
C-1


N
HN
O
HN
HO
N
H
O
O

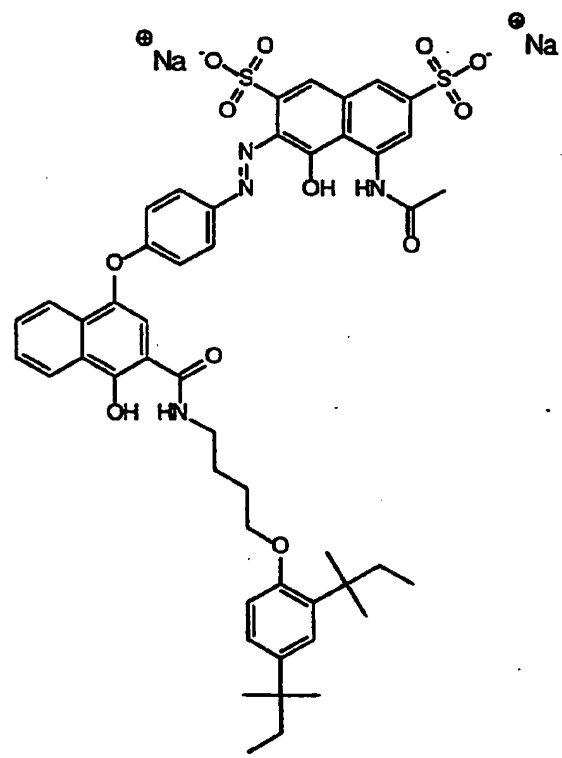
DIR-1


OH
O
NH2
O
O
O
HN
S
N
N
N
N
O=S=O
C16H33

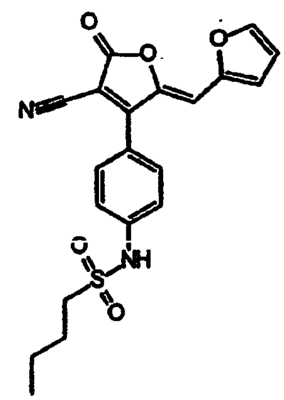
DIR-2



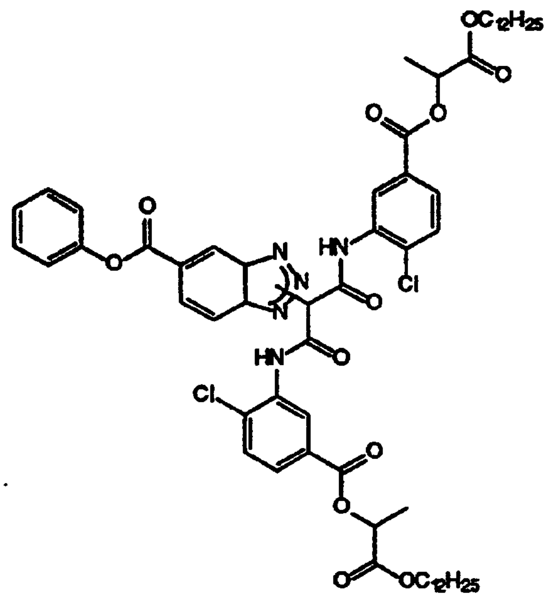
MC-2



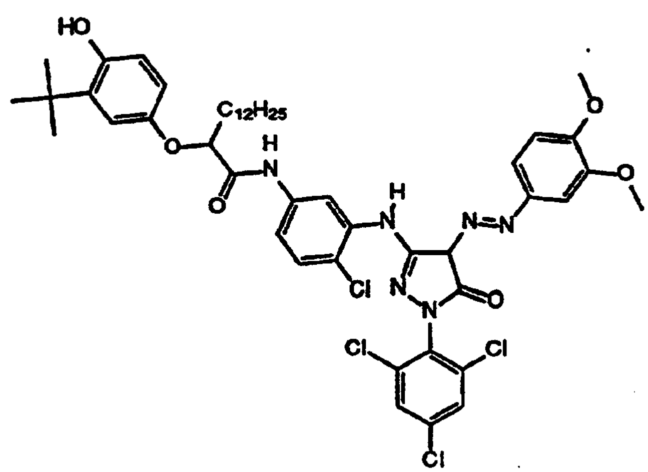
YFD-1



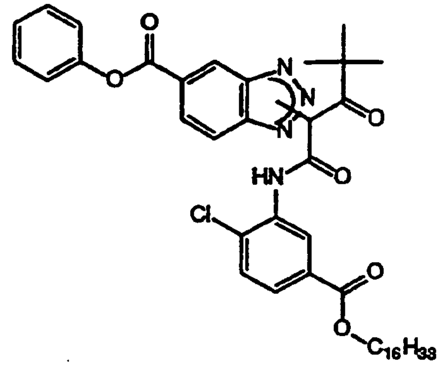
DIR-3



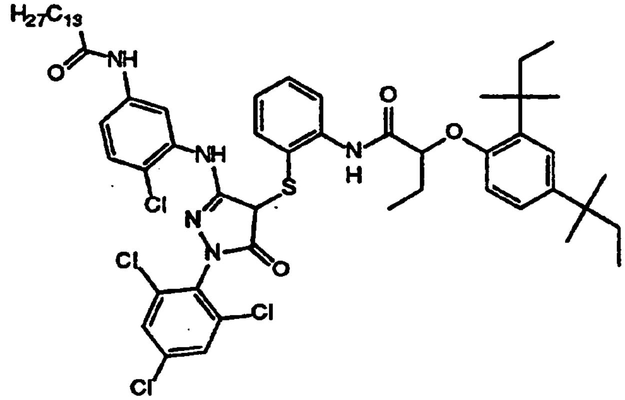
MC-3



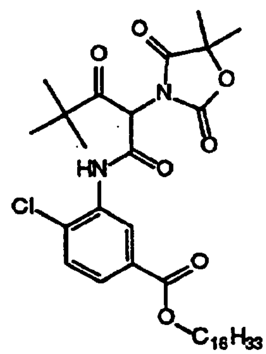
DIR-4



M-1



Y-1

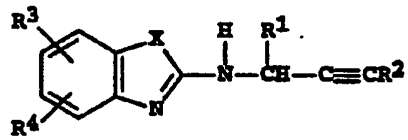


In those examples containing PHR, the compound was added as a water solution to the melts containing the couplers.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

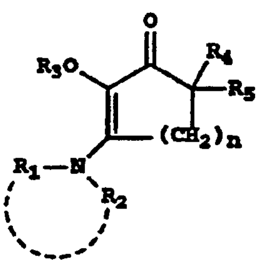
WHAT IS CLAIMED IS:

1. A photographic element wherein at least one layer comprises silver halide grains wherein said grains have a surface iodide of less than 1 mol percent, total grain iodide of about 0.5 to 10 mol percent, said iodide being located in the core of the grains, an alkynylamine compound of Formula I:



I

wherein X represents oxygen, sulfur, selenium, or an unsubstituted or alkyl substituted nitrogen; R^1 represents hydrogen or an alkyl of from 1 to 5 carbon atoms, and R^2 represents hydrogen, or an alkyl, aryl, heteroaryl, carbocyclic or heterocyclic group, and R^3 and R^4 independently represent hydrogen, halogen, or a substituted or unsubstituted alkyl or alkoxy group, preferably one having fewer than 6 carbon atoms, and the reductone of Formula II



II

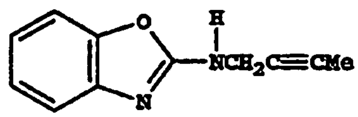
wherein R_1 and R_2 are the same or different, and may represent H, alkyl, cycloalkyl, aryl, or an alkyl group with a solubilizing group such as -OH, sulfonamide, sulfamoyl, or carbamoyl, R_1 and R_2 may be joined to complete a heterocyclic ring, R_4 and R_5 are H, OH, alkyl, aryl, cycloalkyl, or may together represent an alkylidene group, n is 1 or 2 and R_3 is H, alkyl, aryl, or CO_2R_6 where R_6 is alkyl, and

wherein the logarithm of the partition coefficient for the reductone when equilibrated as a solute between n-octanol and water (logP) is less than 0.293.

2. The element of Claim 1 wherein said silver halide grains comprise 1 to 5 mol percent iodide.

3. The element of Claim 1 wherein said silver halide grains have an iodide containing core forming about 70 percent by weight of the total silver halide in the grains.

4. The element of Claim 1 wherein said alkynylamine compound comprises

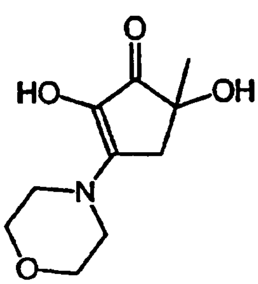
Compound IA: 

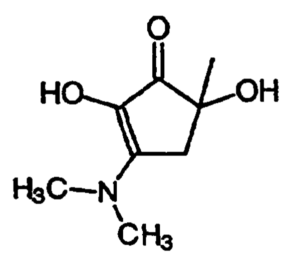
5. The element of Claim 1 wherein said alkynylamine compound comprises a compound wherein R^1 and R^2 are as defined previously, and R^3 and R^4 are hydrogen or methyl, and X is selected from the group consisting of oxygen, sulfur or selenium.

6. The element of Claim 1 wherein in said reductone of Formula II R_1 and R_2 complete a morpholino ring.

7. The element of Claim 1 wherein in said reductone of Formula II R_3 is hydrogen, R_4 is -OH, R_5 is methyl, and n is 1.

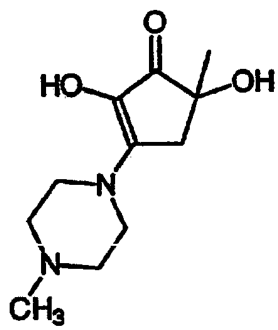
8. The element of Claim 1 wherein said reductone of Formula II is selected from the group consisting of



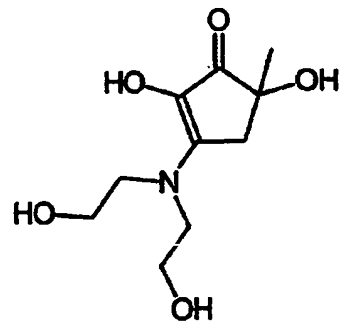


R-3

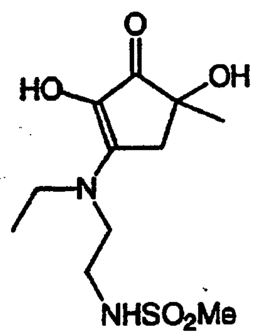
R-2



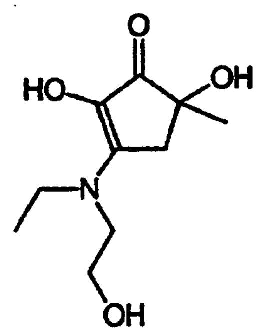
R-4



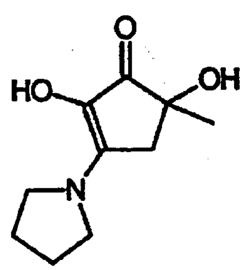
R-5



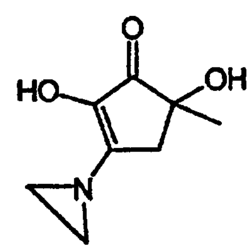
R-6



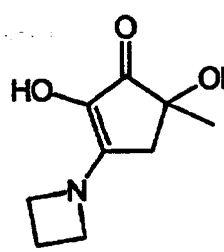
R-7



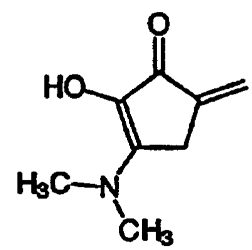
R-8



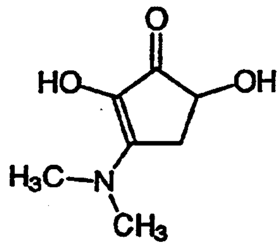
R-9



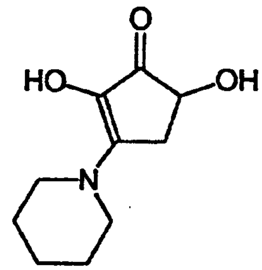
R-10



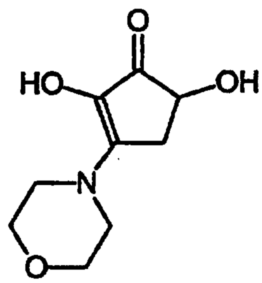
R-11



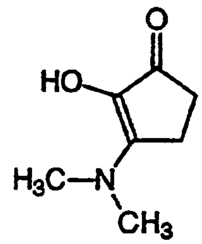
R-12



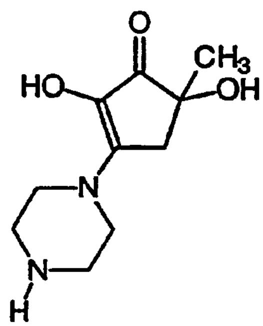
R-13



R-14

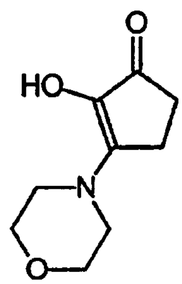


R-15



R-16

and



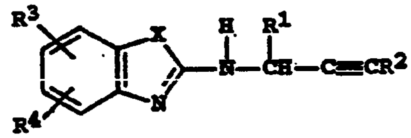
R-17

9. The element of Claim 1 wherein wherein said partition coefficient is between 0.293 and -1.0.

10. The element of Claim 1 wherein said reductone is present in an amount between 0.5 and 50 mg/m^2.

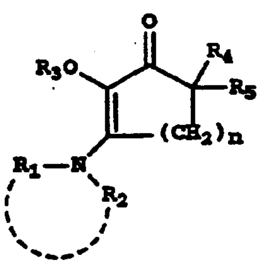
11. A photographic element comprising at least one yellow dye forming blue sensitive layer, at least one cyan dye forming red sensitive layer, and at least one magenta dye forming green sensitive layer wherein at least one of said layers comprises silver halide grains wherein said grains have a surface iodide of

less than 1 mol percent, total grain iodide of about 0.5 to 10 mol percent, said iodide being located in the core of the grains, an alkynylamine compound of Formula I:



I

wherein X represents oxygen, sulfur, selenium, or an unsubstituted or alkyl substituted nitrogen; R^1 represents hydrogen or an alkyl of from 1 to 5 carbon atoms, and R^2 represents hydrogen, or an alkyl, aryl, heteroaryl, carbocyclic or heterocyclic group, and R^3 and R^4 independently represent hydrogen, halogen, or a substituted or unsubstituted alkyl or alkoxy group, preferably one having fewer than 6 carbon atoms, and the reductone of Formula II



II

wherein R_1 and R_2 are the same or different, and may represent H, alkyl, cycloalkyl, aryl, or an alkyl group with a solubilizing group such as -OH, sulfonamide, sulfamoyl, or carbamoyl, R_1 and R_2 may be joined to complete a heterocyclic ring, R_4 and R_5 are H, OH, alkyl, aryl, cycloalkyl, or may together represent an alkylidene group, n is 1 or 2 and R_3 is H, alkyl, aryl, or CO_2R_6 where R_6 is alkyl, and

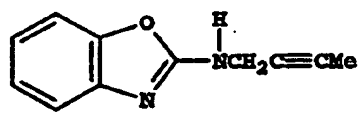
wherein the logarithm of the partition coefficient for the reductone when equilibrated as a solute between n-octanol and water (logP) is less than 0.293.

12. The element of Claim 1 wherein said silver halide grains comprise 1 to 5 mol percent iodide.

13. The element of Claim 1 wherein said silver halide grains have an iodide containing core forming about 70 percent by weight of the total silver halide in the grains.

14. The element of Claim 1 wherein said alkynylamine compound comprises

Compound IA:

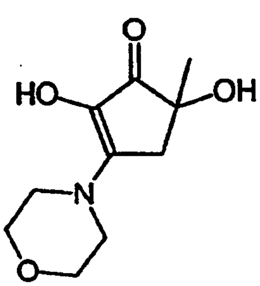


15. The element of Claim 1 wherein said alkynylamine compound comprises a compound wherein R^1 and R^2 are as defined previously, and R^3 and R^4 are hydrogen or methyl, and X is selected from the group consisting of oxygen, sulfur or selenium.

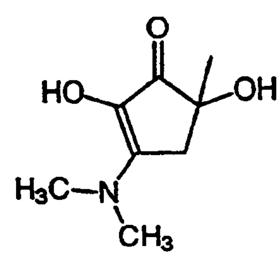
16. The element of Claim 1 wherein in said reductone of Formula II R_1 and R_2 complete a morpholino ring.

17. The element of Claim 1 wherein in said reductone of Formula II R_3 is hydrogen, R_4 is -OH, R_5 is methyl, and n is 1.

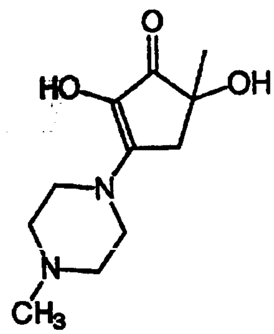
18. The element of Claim 1 wherein said reductone of Formula II is selected from the group consisting of



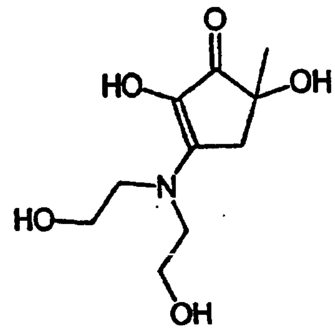
R-2



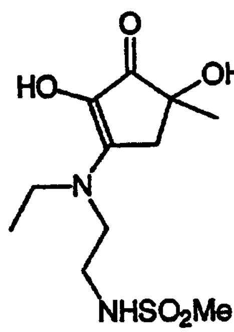
R-3



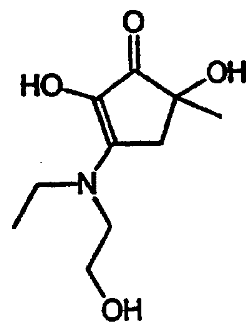
R-4



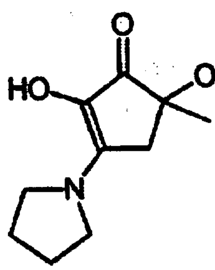
R-5



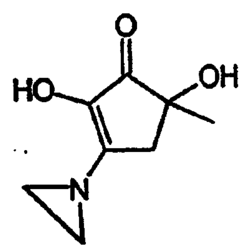
R-6



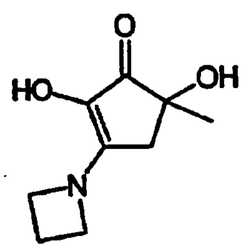
R-7



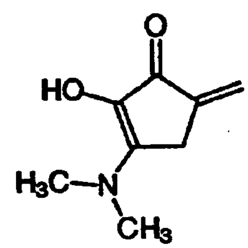
R-8



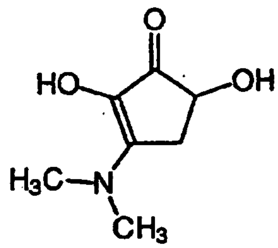
R-9



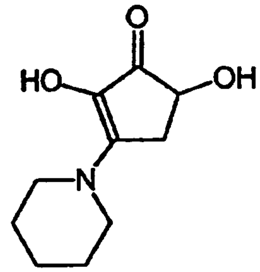
R-10



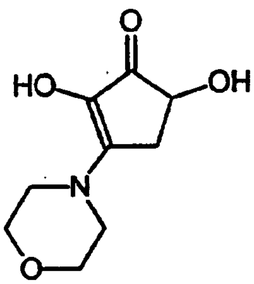
R-11



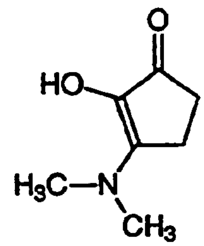
R-12



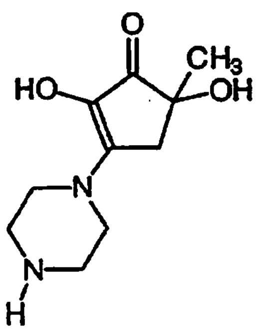
R-13



R-14

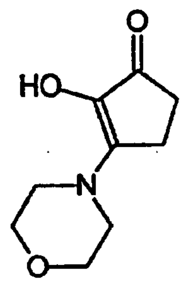


R-15



R-16

and



R-17

19. The element of Claim 1 wherein wherein said partition coefficient is between 0.293 and -1.0.

20. The element of Claim 1 wherein said reductone is present in an amount between 1 and 20 mg/m^2.

21. The element of Claim 11 wherein said at least one layer comprises the yellow dye forming layer.

The Patent Office

- 35 -

Application No:	GB 9818146.4	**Examiner:**	Meredith Reynolds
Claims searched:	1-21	**Date of search:**	22 December 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): G2C (CC19KX,CC19G5, CC19GX)

Int Cl (Ed.6): G03C 1/10,1/34

Other: Online:WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0845705A (Kodak)(pp 4-6, Exs)	
A	US 5389510 (")(Cols 3-6, Exs)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.